Naval Research Laboratory
Washington, DC 20375-5000

NRL Memorandum Report 6569

Chemical Vapor Detection Using Optical Waveguides (OWG)

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October 16, 1989

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): NRL Memorandum Report 6569	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Naval Research Laboratory; 6b. OFFICE SYMBOL (If applicable): Code 6170	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code): Washington, DC 20375-5000	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: Naval Surface Warfare Center; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code): Dahlgren, VA	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): Chemical Vapor Detection Using Optical Waveguides (OWG)

12. PERSONAL AUTHOR(S): Giuliani, J.F.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
FINAL	FROM 10/88 TO 4/89	1989 October 16	13

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Optical waveguide sensors, Optical Reagent coatings characterization

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The work described in this final 6.2 block funding report consists of three main objectives: (1) determination of the most promising reagent coatings which show good selectivity, reproducibility and sensitivity to CW simulants; (2) development of a normalization procedure for applying coating(s) to the OWG capillary glass substrate, and to determine their characteristics such as thickness, refractive index, and temperature dependence; (3) testing of the more promising coatings against live chemical warfare (CW) agents.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL: John F. Giuliani	22b. TELEPHONE (Include Area Code): (202) 767-1399; 22c. OFFICE SYMBOL: Code 6170

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

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CHEMICAL VAPOR DETECTION USING OPTICAL WAVEGUIDES (OWG)

INTRODUCTION

The optical waveguide chemical sensor program for the detection of chemical warfare agents has been funded for the past three years by the Office of Naval Technology, through block funding by the Naval Surface Warfare Center (NSWC), Dahlgren, VA. The goal was to demonstrate that the OWG technology could be applied to develop a low-cost, rugged, light-weight prototype optical agent detector. For field use, a suitable sensor would respond rapidly and selectively to chemical warfare agents in the parts per million concentration range with low false alarm rates.

Work done between October 1986 and September 1988 has already been reported [1]. The effort reported herein is essentially divided into three main objectives: (1) determine the most promising reagent coating or coatings at hand which show good selectivity, sensitivity and reproducibility; (2) develop a procedure for applying coating or coatings to OWG glass substrates, and to determine their characteristics such as thickness, refractive index, reproducibility and stability to CW simulants under environmental testing as a function of temperature under laboratory conditions; (3) test the most promising OWG coating or coatings response to live CW agents.

The optical waveguide transducer used in the evaluation of these reagent film coatings makes use of an hollow capillary glass geometry which had been originally discovered and utilized for the successful characterization of a variety of dye and polymer film studies both in vapor and liquid phase chemical detection [2-11].

Manuscript approved May 18, 1989.

PROMISING OWG REAGENT COATINGS

A preliminary survey of potential reagent coatings which show reversibility, semi-selectivity, and sensitivity in the low parts per million (ppm) range when coated on the waveguide and exposed to CW simulants dimethylmethy phosphonate (DMMP) or N-dimethylacetamide (DMAC) have been narrowed down to two well-characterized polymers [6]. They are polyethylene maleate (PEM) and polyfluoropolyol (PFP) [9]. Their selective response to the above CW physical simulants appear to depend on their close solubility parameter matching with the DMMP and DMAC solubility parameters [9].

FILM COATING METHOD

The next objective was to determine what film coating method would produce a film of good adhesion and uniformity when applied to the outer cylindrical OWG glass surface. There are in general four different coating methods to be considered: (1) dip-coating; (2) spin-coating; (3) spray coating; (4) Langmuir-Blodgett (LB).

The spin-coating and LB coating methods were rejected due to lack of access to appropriate facilities and time and funding constraints required for both preparing glass surfaces and appropriate coating solution preparation. The spray coating procedure, however, was attempted with the PEM material, but the method resulted in a negligible amount of coating actually adhering to the glass as well as producing a highly uneven film over the cylindrical surface. The dip coating method employing a solution of PEM/chloroform produced a rather uniform and relatively good adhesive film on the glass surface at a single dip rate of 0.2 cm/sec [9].

FILM CHARACTERIZATION

The objective for this phase of work involved the determination of the film thickness and the amount of coating which actually adheres to the glass surface in a single dip. Next, the refractive index of the film is determined by means of a total internal reflection technique developed by the author [10]. The thickness for a single dip-coated PEM film on a planar glass substrate was directly measured using a commercial stylus profilometer of ± 5Å resolution. The measured PEM thickness was typically on the order of 122Å ± 5Å for a single pass. From the measured thickness (i.e., 122Å), the amount of PEM coating material on the planar glass plate (0.5 cm x 0.5 cm) was calculated using the empirical equation:

M (mass of film) = t_F (film thickness) x A_P (area of plate) x

P (density of PEM)

$M_{PEM} = (1.22 \times 10^{-5}\text{cm})\ (0.25\ \text{cm}^2)\ (1.353\ \text{gm/cm}^3)$

$M_{PEM} = 4.1 \times 10^{-6}$ grams = 4.1 μ grams

This mass was independently checked by directly weighing a single dip-coated PEM film on the OWG 9 cm x 1.1 mm x 0.8 mm capillary employing a microbalance (± 2 μg accuracy). These measurements indicated that approximately 5 μ grams of coating is present on the capillary surface. This is in good agreement with the profilometer thickness measurements which were made on the planar glass substrate. Film coating by the dipping method was also attempted for the PFP/chloroform solution. The resulting coatings were rather poor due to the poor surface adhesion of this low surface tension material to the capillary surface. No attempt was made to determine the PFP film thickness, nor mass of material on the capillary surface. Although the PFP films are of poor quality they are still useful for detecting DMMP and DMAC vapors.

Refractive index measurements show that the resultant PEM and PFP films were in the order of 1.484 ± 0.002, and 1.413 ± 0.015, respectively, at room temperature, using a HeNe laser source (λ = 632.8 nm).

REPRODUCIBLE COATING AND VAPOR RESPONSE STUDIES FOR MULTIPLE OWG SENSORS

A statistical study was made in which a single pass PEM and PFP dip-coated film was applied to 8 separate capillary sensors which were then exposed to a single vapor at a fixed concentration at room temperature and constant humidity conditions (20% RH). For these studies the objectives were to measure the standard variation in response to the vapor of fixed dilution concentration from one coated capillary to another, and the standard variation for a single-coated sensor to the same vapor concentration. Acetone vapor at a concentration level of 122,000 ppm and DMMP concentration of 200 ppm were used to determine the PEM and PFP films' responses in these studies. An average of thirty vapor exposures for each sensor was taken both for each separate PFP and PEM-coated OWGs as well as for a single PFP and PEM coating exposed to the same fixed acetone and DMMP vapor concentrations. The results show that the standard deviation from one coated PEM sensor to another for the 8 separate coated sensors is 25% for both exposure to acetone and DMMP vapors, and the standard deviation for any one PEM or PFP coated device to the fixed acetone and DMMP dilution concentrations is ± 5%. The angular alignment variations resulting from the replacement of one coated capillary tube for another, incorporated into the LED/phototransistor system, is responsible for most of the 25% variation. However, this is an engineering problem which can be easily solved by a tighter tolerance on the optical coupling connections.

OWG SENSOR RESPONSE TO VAPORS AS A FUNCTION OF TEMPERATURE

For these experiments, a single PEM- and PFP-coated sensor was exposed to DMMP and acetone vapors and their responses were measured as a function of sensor temperature over a range of 20°C to 50°C. All the response data was normalized to 1000 μmoles/liter correcting for the differences in vapor pressure between DMMP and acetone vapors. In this normalization procedure, the parameters determined at a particular temperature and fixed gas/vapor flow rate of 90 μL/min are the difference in measured photo detector voltage between the vapor/nitrogen carrier gas signal (Δv) and nitrogen carrier gas voltage (v), respectively. Since the reference nitrogen carrier baseline signal voltage changes as a function of temperature, as does Δv, the ratio $^{\Delta v}/_{v}$ corrects for these baseline variations.

Moreover, since the saturated vapor pressures of acetone and DMMP are significantly different from each other it is necessary to correct the ratios by normalizing the vapor pressures for DMMP and acetone on a per 1000 μmole/liter basis. Hence, the ratio $^{\Delta v}/_{v}$ of a vapor is divided by a normalization correction which is the ratio of its vapor pressure at temperature T, to its vapor pressure at STP times the ratio of its molecular weight to its molar volume at STP. These results are shown in Figures 1 and 2 where the normalized response $(^{\Delta v}/_{v})/1000\ \mu$ moles/liter is plotted as a function of the reciprocal temperature $(10\ ^{3}/_{°K})$, on a semi-log graph. The linear graph for both sensors indicate the expected Arrhenius type temperature response which indicates that both the PEM and PFP film sensors respond more strongly to DMMP than to acetone as predicted from solubility parameter matching data [9]. The slope of the nitrogen carrier baseline voltage (v) decreases by only 1% of the vapor response slopes indicated in Figures 1 and 2

over the indicated temperature range. Hence, the baseline voltage shifts do not produce a significant contribution to the vapor response between 20°C and 50°C.

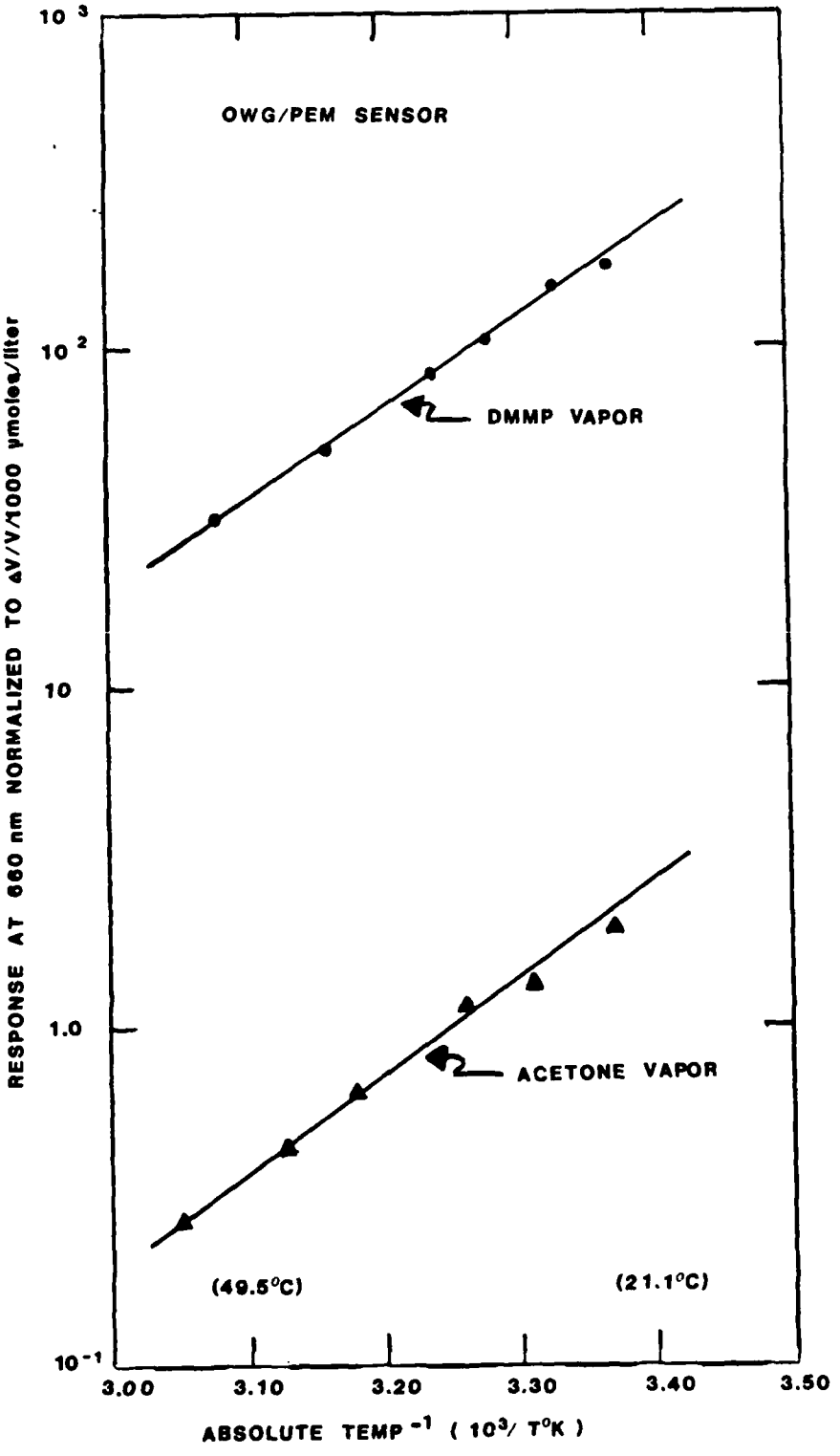

Figure 1. OWG Sensor Response to Vapors as a Function of Temperature

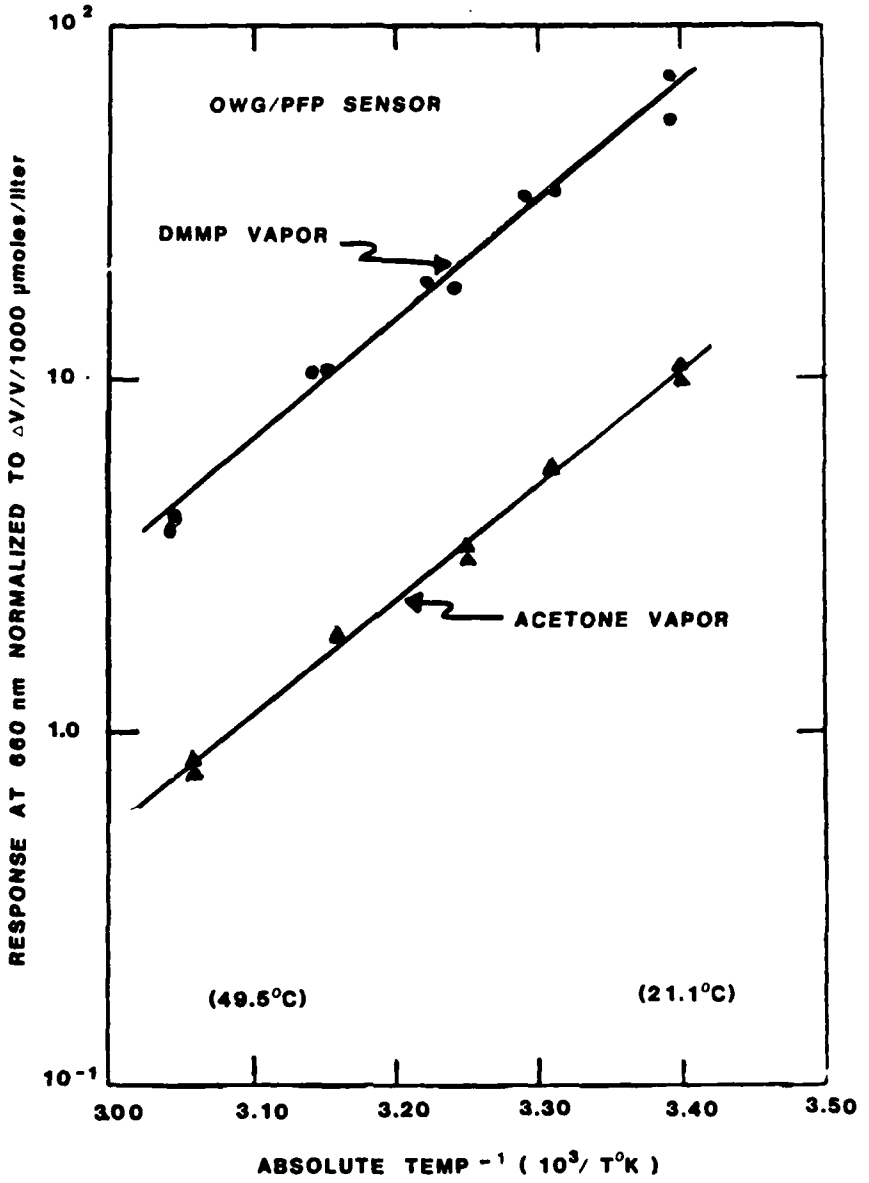

Figure 2. OWG Sensor Response to Vapors as a Function of Temperature

LIVE AGENT TESTING

Due to the lack of funding only the PEM coated OWG sensor was tested against two live chemical warfare agents, GB and HD. Preliminary room temperature tests indicated detection-levels as low as 16 ppm for GB and 8 ppm for HD in air, respectively. This work had been sub-contracted out to CRDEC, Aberdeen Proving Ground, Edgewood, MD, and had been reported in an earlier October 1986 to September 1988 NSWC sponsor report.

SUMMARY

The studies reported here completes the 6.2 ONT block funding for the optical waveguide (OWG) chemical sensor program. A prototype NRL MK-II optical sensor has been built, which replaces the MK-I device [12]. For the MK-II sensor, the 20 μW LED source is replaced with a 2000 μW LED source, and the phototransistor is replaced in the MK-I with a wide bandwidth photo-diode detector. These improvements should result in a factor of 10 to 100x increase in vapor detection sensitivity with selective reagent film coatings.

ACKNOWLEDGEMENTS

The author wishes to thank NSWC, Dahlgren, VA for their support of this three-year effort, and to Paul P. Bey, Jr., for his technical assistance in the development of the prototype sensors.

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